

## SHORT COMMUNICATIONS

### VIBRATIONAL SPECTRA OF AQUATUNGSTEN (VI) OXIDE ( $\text{WO}_3 \cdot \text{H}_2\text{O}$ )

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AQUATUNGSTEN (VI) oxide ( $\text{WO}_3 \cdot \text{H}_2\text{O}$ ) is one of the very few hydrated oxides with a water molecule directly bonded to a metal atom<sup>1</sup>. No detailed vibrational study of this compound has been done so far. In the present communication, vibrational analysis of  $\text{WO}_3 \cdot \text{H}_2\text{O}$  has been carried out to understand the nature of the co-ordination between the tungsten and oxygen atoms.

The Raman spectrum of Analar grade  $\text{WO}_3 \cdot \text{H}_2\text{O}$  was recorded in the Stokes' region of the green line 5145 Å (power 200 mW) using a Spex Ramalog 1401 double monochromator equipped with a Spectra Physics model 165 Ar<sup>+</sup> laser. As there is a possibility of the sample getting dehydrated, the spectrum was recorded in six steps, each time introducing a capillary tube filled with new sample. The IR spectrum in the region 200–4000  $\text{cm}^{-1}$  was

obtained on a Perkin-Elmer 983 spectrophotometer with the sample prepared as KBr pellet.

The tetramolecular orthorhombic unit cell (Pmnb) of  $\text{WO}_3 \cdot \text{H}_2\text{O}$  is characterized by distorted octahedral units of tungsten atoms co-ordinated to five oxygen atoms and a water molecule<sup>1</sup>. Hence vibrational assignments have been carried out on the basis of vibrations due to  $\text{WO}_6$  octahedron and water molecule. The lower site symmetry of the octahedra may lead to anisotropic crystal field, causing the inactive modes to become active, removal of degeneracies of normal modes; and shifting of the frequencies of non-degenerate modes.

The vibrational assignments are given in table 1. The splitting of the non-degenerate  $\nu_1$  mode of  $\text{WO}_6$  is due to correlation field effect. A large splitting of about 110  $\text{cm}^{-1}$  is observed for the  $\nu_3$  mode due to site symmetry and correlation field effects. This large splitting of the  $\nu_3$  mode and shifting of the bending modes  $\nu_4$  and  $\nu_5$  to high frequencies are indicative of a considerably distorted<sup>2,4</sup>  $\text{WO}_6$  octahedron. The appearance of inactive modes also supports this. Two sets of frequencies have been observed for the vibrations of O–H bonds. Hence hydrogen bonds of two different strengths are evident, as suggested from structural studies<sup>1</sup>.

The strong IR band at 1400  $\text{cm}^{-1}$  is assigned to the O–H . . . O deformation mode<sup>5</sup>. Even though the librational modes of water fall within the region

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Table 1 Vibrational assignments for  $\text{WO}_3 \cdot \text{H}_2\text{O}$

Raman ( $\text{cm}^{-1}$ )	IR ( $\text{cm}^{-1}$ )	Assignments
3398 (m), 3372 (br)	3000–3300 (br)	$\nu_3$ $\text{H}_2\text{O}$
3267 (m), 3214 (m)	3000–3300 (br)	$\nu_1$ $\text{H}_2\text{O}$
1652 (br), 1620 (br)	1650–1610 (br)	$\nu_2$ $\text{H}_2\text{O}$
	1400 (vs)	O–H . . . O deformation
959 (sh), 952 (vs), 931 (s)	950 (m), 927 (m)	$\nu_1$ $\text{WO}_6$
884 (s), 857 (s), 823 (s),	880 (s, br), 858 (m)	
816 (s), 778 (s), 771 (w)	810 (m), 770 (br)	$\nu_3$ $\text{WO}_6$
744 (w), 733 (m), 726 (s)	730 (w), 705 (w)	$\nu_2$ $\text{WO}_6$
683 (br), 648 (br), 560 (br)	675 (w), 600–540 (br)	Librations of $\text{H}_2\text{O}$
506 (s), 492 (w), 455 (s),	525 (m), 505 (m)	
444 (s), 421 (m)	455 (w), 438 (w)	$\nu_5$ $\text{WO}_6$
397 (m), 392 (m),	335 (w)	
320 (m), 307 (s)	314 (m)	$\nu_4$ $\text{WO}_6$
287 (w), 246 (m), 217 (w),		
204 (m), 182 (s), 106 (m)		External modes

s, strong; br, broad; m, medium; w, weak; vs, very strong; s, br, strong broad.

of the internal modes of  $WO_6$ , one can distinguish the weak bands due to the water molecule. Assignment of bands due to external modes is difficult in a powder spectrum.

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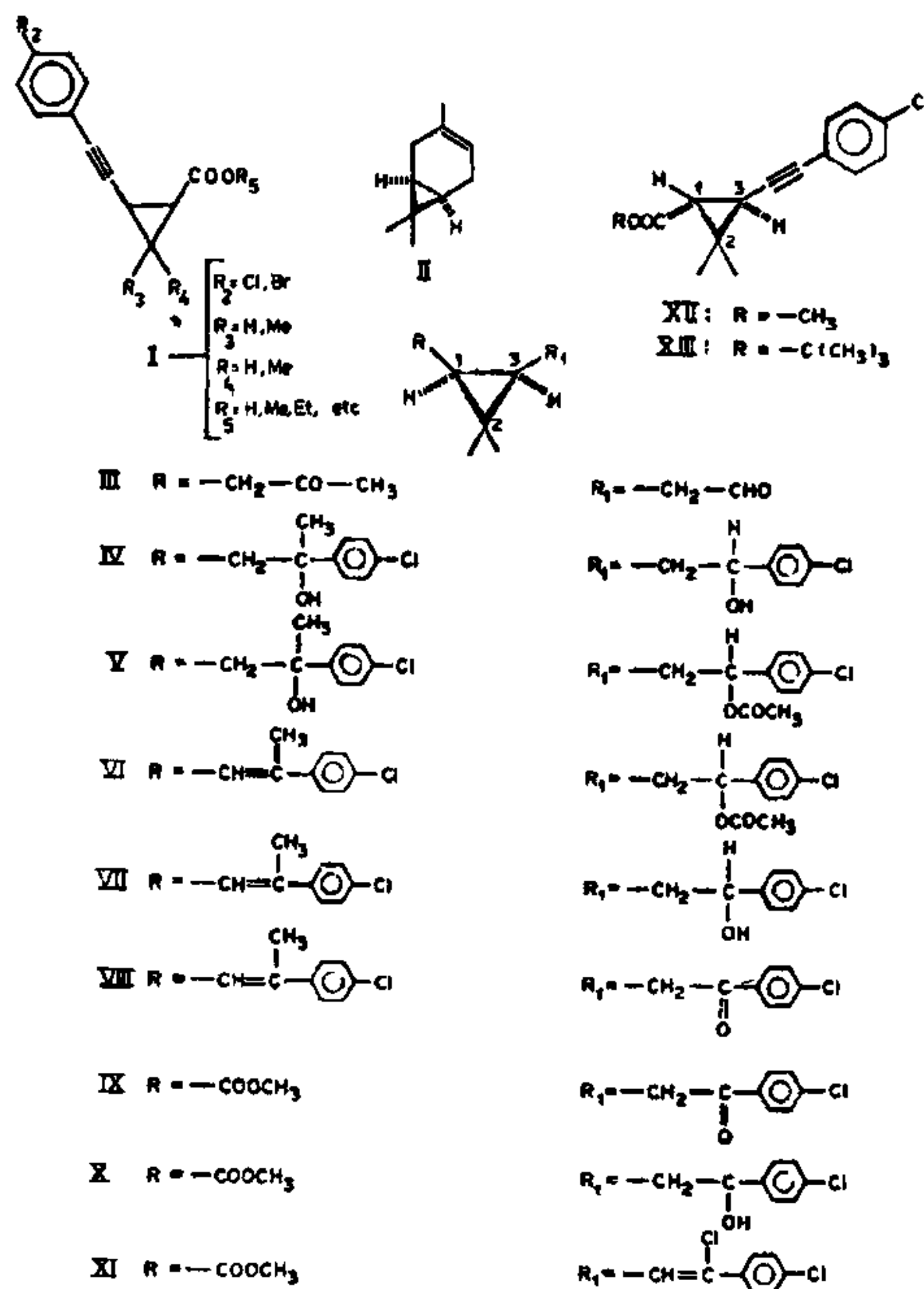
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### STEREOSPECIFIC SYNTHESIS OF METHYL/*t*-BUTYL (+)-1*R*-*TRANS*-2, 2-DIMETHYL-3-(2-*p*-CHLOROPHENYLETHYNYL)CYCLOPROPANECARBOXYLATES FROM (+)-3-CARENE

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IN an earlier communication<sup>1</sup>, we reported the synthesis of 3-phenoxybenzyl (+)-1*R*-*trans*-2, 2-dimethyl-3-(2-*p*-chlorophenyl-2-chlorovinyl/2-*E*-*p*-chlorostyryl/2-*p*-chlorophenylethynyl)cyclopropanecarboxylates. Some of these esters have been already reported to possess insecticidal, acaricidal and ectoparasiticidal activities. Kishida *et al*<sup>2</sup> have synthesized substituted 2-ethynylcyclopropane-1-carboxylic acid esters of type I, patented for their insecticidal, herbicidal, anti-inflammatory properties and also as hypoglycemic agents. In this communication, we report an alternative stereospecific route for the optically active esters of type I, viz. XII and XIII from (+)-3-carene (II).

Grignard reaction on ketoaldehyde (III), obtained from (+)-3-carene (II), using *p*-chlorophenylmagnesium bromide (2.5 mol), gave a diastereomeric mixture of diols (IV, 72%),  $C_{22}H_{26}O_2Cl_2$ , as a thick liquid identified by spectral data. IR<sup>\*\*</sup>: 3380 (OH), 1598 (aromatic). PMR ( $CDCl_3$ ): 0.44 (2H, *m*,  $C_1$  and  $C_3$  H), 0.64, 0.70, 0.80, 0.88, 0.96, 1.04 (6H, *s* each, cyclopropanemethyls of diastereomers), 1.56



(7H, *s* overlapping a multiplet,  $CH_2$  at  $C_1$  and  $C_3$  and tertiary methyl), 2.64 (2H, *s*, exchangeable with  $D_2O$ , hydroxy H), 4.72 (1H, *m*, benzylic H) and 7.36, 7.45 (8H, *s* each, aromatic H).

The hydroxymonoacetate (V) prepared from IV, afforded, on dehydration (pTSA/benzene), unsaturated acetate (VI, 90%) as a mixture of diastereomers,  $C_{24}H_{26}O_2Cl_2$ . IR: 1735, 1232 (acetate), 1598 (aromatic), 820 ( $-CH=C-$ ). PMR ( $CDCl_3$ ): 0.68 (1H, *m*,  $C_3$  H), 0.84, 1.00, 1.06, 1.14 (6H, *s* each, cyclopropanemethyls of diastereomers), 1.32 (1H, *m*,  $C_1$  H), 1.8 (2H, *m*,  $CH_2$  at  $C_3$ ), 2.04 (6H, *brs*, vinyl and acetate methyls), 5.35–5.74 (2H, *brm*, olefinic and benzylic H of diastereomeric *E* and *Z* isomers) and 7.28, 7.36 (8H, *s* each, aromatic H).

The corresponding unsaturated alcohol (VII) obtained from VI by saponification (KOH, MeOH) gave, on Jones oxidation, the expected ketone (VIII, 76%),  $C_{22}H_{22}OCl_2$ .  $[\alpha]_D^{25} + 19.5^\circ$  (*c*, 0.5,  $CHCl_3$ ).

\*Satisfactory elemental analysis has been obtained for all the compounds reported.

\*\*IR bands expressed in  $\nu$  ( $cm^{-1}$ ) and PMR chemical shifts in  $\delta$  (ppm) with TMS as internal standard.